

HIGH ENERGY SUPPLY APPARATUS, METHOD OF FORMING CRYSTALLINE FILM AND METHOD OF MANUFACTURING THIN FILM ELECTRONIC DEVICE

## BACKGROUND OF THE INVENTION

#### 1. Field of Invention

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The invention relates to a high energy supply apparatus such as a laser irradiation apparatus, a method of forming a crystalline film by using the high energy supply device, and a method of manufacturing a thin film electronic device including a crystalline film formed by the method.

#### Description of Related Art

As screen size and liquid crystal display (LCD) resolution increase, LCD driving systems are transferred from simple matrix systems to active matrix systems, thereby enabling the display of large volumes information. The active matrix systems enable LCD devices to have more than hundreds of thousands of These systems include a switching element, such pixels. a thin film transistor (TFT), for each pixel. Transparent insulating substrates, such as a fused quartz plate, a glass plate, which enables transmission type displays are used as substrates for various types of LCD. devices.

A semiconductor film of amorphous silicon (a-Si) or polycrystalline silicon (poly-Si) is generally used to form an active layer for the TFT. When both the pixel switching element and the driving circuit are integrally formed using a TFT, it is necessary and essential to use silicon exhibiting a polycrystalline high When a polycrystalline silicon film is utilized as the active layer, the TFT is generally formed by using a fused quartz plate as a substrate in a manufacturing method referred to as a high-temperature process in which the maximum temperature exceeds 1000°C. In this case, the film mobility of the polycrystalline silicon is approximately 10 cm $^{-2} \cdot V^{-1} \cdot S^{-1}$  to 100 cm $^{-2} \cdot V^{-1} \cdot S^{-1}$ . On the

other hand, when an amorphous silicon is utilized to form the active layer, the highest temperature of the process is as low as approximately 400°C and a glass substrate is thus generally used. The mobility of the amorphous silicon film is approximately 0.1 cm $^{52} \cdot V^{-1} \cdot S^{-1}$  to 1 cm $^{52} \cdot V^{-1} \cdot S^{-1}$ .

Advances in enlargement of LCD display screens and reduction in cost require the use of a low-cost glass plate as an insulating substrate. However, as described above, amorphous silicon film is significantly inferior to polycrystalline silicon film in electrical properties, and is subject to problems, such as having a operation speed, for example. On the other hand, the silicon TFTproduced the polycrystalline by temperature process includes a fused quartz plate, and thus is subject to the problem of increasing LCD cost. Therefore, there is strong demand for a technique for forming a thin film semiconductor device which includes a crystalline semiconductor film, such as a polycrystalline silicon film, as an active layer formed on a usual glass In the case of a conventional large glass substrate. substrate which has a high mass productivity, the highest temperature of the process is limited to approximately in order to avoid deformation of the 400°C or less This is referred to as a "low-temperature substrate. TFT" and is now under development. process polv-Si Eventually, the most important technical problem of the low-temperature process poly-Si TFT lies in how to form an excellent crystalline film by a processing temperature of 400°C or less, i.e., how to improve an apparatus for forming a good crystalline film. Solution to such a problem enables not only the formation of a good TFT and comprising this TFT but also significant LCD improvements in performance of all electronic devices such as solar cells and semiconductor device circuits, which are formed by using crystalline films. At the same time, this enables a further reduction of the cost.



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important technical most problem development of a low-temperature process poly-Si TFT lies in forming an excellent crystalline film utilizing processing temperature of 400°C or less, i.e., improve an apparatus for forming a good crystalline film. Solving the aforementioned difficulties development of a good TFT and LCD and also significantly improves the performance of all electronic devices, such as solar cells and semiconductor device circuits, which are formed by using crystalline films. At the same time, this further reduces the cost.

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Conventionally, as disclosed in SID (Society for **`**93 P. 387 Information Display) Digest (1993).crystalline film is formed at a low temperature, and a thin film electronic device including the film is formed. silicon film is formed polycrystalline crystalline film, and a TFT is formed as the thin film The crystalline film is formed by electronic device. an a-Si film of 50 nm by a low-pressure depositing chemical vapor phase deposition process (LPCVD process) using monosilane ( $SiH_4$ ) as a raw material at a deposition temperature of 550°C, and then applying a laser beam to Although not disclosed herein, the formed a-Si film. irradiation of the laser beam is carried out by the laser irradiation apparatus 101 shown in Fig. 1. irradiation apparatus 101 includes a laser light emission source 102 and a laser irradiation chamber, a substrate having a material 103 to be irradiated such as the a-Si film which is placed on the surface thereof disposed on a stage 105 provided in the laser irradiation In the laser irradiation chamber, incident window is provided which includes quartz glass at a position opposite to the stage so that a laser beam 107 is incident through the laser incident window 106. The distance between the laser incident window and the substrate 104 is generally approximately 1 cm. The material to be irradiated is irradiated with a laser beam

at a stage temperature from room temperature to about 400°C under vacuum pressure to atmospheric pressure.

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After the poly-Si film including a crystalline is obtained as described above, the thin film film electronic device (TFT) is formed utilizing the poly-Si Specifically, after the poly-Si film is processed to a desired shape, an oxide film which functions as a gate insulating film is deposited by a PECVD process. gate electrode is formed on the gate insulating film by using tantalum (Ta), and then a source and a drain for a transistor are formed in a self alignment manner implanting donor or acceptor impurities into the polycrystalline silicon film using the gate electrode as Impurities are implanted by an ion doping method using a mass non-separation type implantation apparatus and phosphine ( $PH_3$ ) and diborane ( $B_2H_6$ ) as raw material gases which are diluted with hydrogen. The ions injected are activated at 300°C. The insulating layer is then deposited, and electrodes and wiring are formed by using indium tin oxide (ITO) and aluminum (Al) to complete a TFT.

conventional method for obtaining Another crystalline semiconductor film at a low temperature is disclosed in Japanese Patent Laid-Open No. 7-99321. a-Si film is formed and then irradiated with a laser beam to obtain a crystalline film. Irradiation of the laser beam is carried out under vacuum pressure or in an inert In fact, the same publication discloses gas atmosphere. "At least the surface layer of the following. semiconductor thin film formed on the substrate is melted and recrystallized under reduced pressure or in an inert gas atmosphere, and the substrate (1) having the melted and recrystallized semiconductor film formed thereon is transferred to the step of forming an insulating film on the melted and recrystallized semiconductor film while being maintained under reduced pressure or in an inert gas atmosphere." A TFT is formed by a manufacturing method similar to the first conventional method described above using the obtained polycrystalline silicon film. Eventually, in the conventional methods, a crystalline film is obtained by irradiating a silicon film with a laser beam using the laser irradiation device shown in Fig. 2 under vacuum pressure to atmospheric pressure or in an inert gas atmosphere.

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However, the aforementioned conventional methods have the following problems:

- 10 (1) Irradiation under atmospheric pressure contamination of the crystalline film causes with impurities, such as oxygen and nitrogen or Particularly, when the crystalline film includes semiconductor or a metal, contamination with oxygen or dust creates significant deterioration in the physical 15 properties of the thin film formed;
  - (2) The gas frequently used in crystallization under an inert gas atmosphere is nitrogen. Since nitrogen is highly reactive with semiconductors such as silicon and with metals such as tantalum, a high-purity crystalline semiconductor film and crystalline metallic film cannot be obtained;
  - (3) Irradiation under a vacuum necessitates that a laser irradiation chamber with high sealing performance is provided, and a large scale evacuation device such as a turbo-molecular pump is added to a laser irradiation apparatus. This increases the cost of a thin film electronic device which includes a crystalline thin film and decreases productivity;
- 30 (4)In melt crystallization, the component elements of the melted material irradiated with a laser beam are invariably scattered or evaporated. This particularly pronounced in phenomenon is irradiation under vacuum because melting under a vacuum 35 causes the formation of a deposited film. As a result, a film of the material irradiated with a laser beam is laser incident window of the formed on the laser

irradiation apparatus. Fig. 1 shows a scattered molecule 108 in this state. Evaporation of the material 103 to be irradiated and the formation of a film on the laser incident window represent attenuation of the laser energy applied to the material to be irradiated at each time of laser irradiation. Namely, the conventional methods are incapable of obtaining a crystalline film having good characteristics and instead possess large variations in film quality;

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- 10 (5) When high energy is supplied to the material to be irradiated by laser irradiation to progress melt crystallization, as the energy supplied increases, the quality of the crystalline film is improved. However, in vacuum irradiation, the problem described in (4) above becomes significant as the supplied energy increases. This makes it substantially impossible to increase the energy supplied for vacuum irradiation and improve the quality of the crystalline film obtained; and
- In laser irradiation under vacuum or in an 20 inert gas atmosphere, at the end of melt crystallization by irradiation where the material to be irradiated with a laser beam is transferred from a solution state to a crystal solid state, the surface is reconstructed to minimize the surface energy and many chemically active unpaired bonding electrons remain on the surface. 25 The reconstructed surface having unpaired bonding electrons has a structure completely different from that of the internal crystal, and thus exhibits an energy band diagram significantly different from that of the internal 30 Many electronic devices employ both film film and а metallic thin semiconductor thin For example, field effect transistors surfaces. include a semiconductor thin film where an inveresion layer is formed on the surface of the semiconductor to control the transfer process of electrons and holes in 35 the semiconductor. In metal wiring, of course, a current flows through the surface of the metallic thin film.

a device (for example, a mirror and a metal catalyst) which employs the optical properties or chemical properties of a thin film, the device characteristics are determined by the surface.

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If the important surface having unpaired bonding electrons is greatly different from the inside due to reconstruction, the physical properties of the surface greatly change (generally deteriorate). in a FET that includes a semiconductor thin film, the mobility in the inversion layer is decreased to several tens to several % of the mobility of the inside of the semiconductor according to the surface state. same phenomenon is observed in a metallic thin film (for example, the electric conductivity of the metallic thin film changes). As described above, control of surface plays an important part in obtaining film. However, in а conventional crystalline crystallization method, such control is not sufficiently obtained, and thus a superior crystalline film cannot be obtained. Further, the characteristics crystalline film vary greatly with variations in reconstructed surface at state of the each melt crystallization.

### SUMMARY OF THE INVENTION

Accordingly, the object of the present invention is to solve the above problems and provide a high energy supply apparatus such as a laser irradiation apparatus, a method of forming a good crystalline film using the high energy supply apparatus at a relatively low temperature, and a method of manufacturing a thin film electronic device including the crystalline film formed by the disclosed method.

In the first step of the invention, thin films of a semiconductor material such as silicon and a metal such as tantalum are deposited on various substrates. In the second step, at least the surface layers of the thin films are partially melted and then crystallized through a cooling solidification process (hereinafter "melt crystallization") to form various crystalline films. Substrates to which the invention can be applied and thin films are described in detail below.

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Crystalline films include films in a single crystal state, a polycrystal state or a mixed crystal state wherein a crystal and an amorphous material are mixed. Melt crystallization is achieved by supplying high energy, such as a laser beam, to the thin films. Possible forms of high energy include electromagnetic waves such as light, X-rays, and gammer rays; charged particle flows such as proton rays, electron rays, and alpha rays, and neutral elementary particle rays such as neutron rays and neutral meson rays.

Elementary particle rays are advantageous because high energy can simply be supplied to the thin films through strong or weak interaction. Even when the thin films have low electric conductivity, neutral elementary particle flows containing electromagnetic waves (photon) do not apply unnecessary charges to the thin films and thus do not electrically damage the thin films during supply of high energy. This is particularly important when the thin films are intrinsic or nearly intrinsic semiconductor films, because these thin films have low electric conductivity. The charged particle flows have the advantage that they can easily be formed by generating a plasma of atoms, and that the direction of the charged particle flows can easily be controlled. view of the ease of handling, including formation and direction control and safety, the optimum high energy material is electromagnetic waves with a wavelength from about 10 nm to about 10 µm, i.e., light. Light can be classified into laser beams and nonlaser beams, both of which can be used as forms of high energy.

In the second step, metal crystallization proceeds in a mixed gaseous atmosphere containing hydrogen molecules  $(H_2)$  and an inert gas; a hydrogen

halide such as hydrogen fluoride (HF), hydrogen chloride (HCl) and an inert gas; an inert gas and an acid such as nitric acid (NHO<sub>3</sub>) or sulfuric acid (H<sub>2</sub>SO<sub>4</sub>); an inert gas and a gas containing as a hydride of the component element of a thin film of a semiconductor, such as silane  $(SiH_4, Si_2H_6)$ . As the inert gas, nitrogen  $(N_2)$ , single rare gases such as helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe); mixed gases containing these chemically inert for all gases thin films melt crystallization and to mixed subjected gases containing these gases can be used.

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crystallization of a thin film in an atmosphere containing an inert gas and hydrogen has the advantages that it significantly decreases contamination of the thin film with impurities such as oxygen and dust particles floating in air and improve the purity of the crystalline film formed as compared with crystallization For semiconductor films and metallic in atmosphere. films, it is well known that as the amounts of impurities in the film decreases, the physical properties of the film such as mobility are improved. For semiconductor intentionally added impurities are in trace amounts of about 1 x  $10^{18}$  cm<sup>-3</sup> or less to control the physical properties of the films. From this viewpoint, it is important to obtain a high-purity semiconductor Contamination of the thin films from air becomes a more serious problem in melt crystallization than crystallization (solid phase crystallization or "SPC") in This is because in a liquid state where a solid state. processing temperature is higher than that in solid phase crystallization, impurities diffuse and chemically react with the components of the thin films at higher Therefore, control of the atmosphere in metal crystallization is more critical than in solid phase crystallization.

It is important for reasons discussed below that the atmosphere for progressing metal crystallization

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When a thin film is melted by contains hydrogen. supplying high energy and then solidified to a crystal, the adjacent atoms in the thin film combine with each other to form a regular crystal structure. However, on the upper half of the surface, no bonding atoms are Hence, in melt crystallization under vacuum or in an inert gas, unpaired bonding electrons combine with each other to reconstruct the surface on the surface of structure of the the thin film. The reconstructed surface is greatly different from the inner structure of the crystal, causing a change in the band structure. addition, large stress is present in the reconstructed This stress causes lattice distortion which affects the surface crystalline film. A change in the band structure changes the concentrations of electrons and the lattice distortion decreases and holes, mobility of electrons and holes. In addition, bonding of atoms on the surface produces unpaired bonding electrons. These electrons are chemically active and thus react with water and oxygen in the air also absorb dust when the exposed to air the film is at end thin crystallization process. In addition, the presence of unpaired bonding electrons produces interfacial levels and scattering centers of electrons and holes, thereby deteriorating the mobility of electrons and Therefore, the reconstructed surface has various adverse effects on the physical properties of the thin films.

In the method of forming a crystalline film of melt crystallization of the thin film the invention, containing atmosphere proceeds in an hydrogen. Therefore, the unpaired bonding electrons which appear on the thin film surface during the cooling solidification process are terminated by various types of hydrogen atoms (hereinafter "hydrogen termination") contained in The reconstruction of the surface is thus atmosphere. avoided, and at the same time, the total number of the unpaired bonding electrons is significantly decreased.

Therefore, the crystalline film obtained accordance with the invention has high purity extremely close structure to the inner surface crystalline structure. As a result, the metallic surface intrinsic physical simply reflects the properties itself, and the semiconductor metal possessed by a surface also exhibits the physical properties of the For example, when a FET (so-called TFT) semiconductor. including a polycrystal semiconductor thin film is formed according to the invention, because the mobility hardly due the reconstructed surface, deteriorates to effective mobility is significantly improved, compared to the effective mobility of a TFT formed by conventional techniques. The mobility value also does not change with substrates and lots.

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Melt crystallization in a mixed gas atmosphere containing hydrogen molecules and an inert gas, does not introduce impurities into a crystallized film of a metal therefore, high-purity or semiconductor, and а crystallized film terminated with hydrogen is obtained. During melt crystallization of a semiconductor film of silicon under an atmosphere containing a hydrogen halide and an inert gas, the crystallized semiconductor film is securely terminated with hydrogen because that the halide reacts relatively easily with the semiconductor film. This is particularly effective for metallic thin films. It is ideal for melt crystallization to progress in a mixed gaseous atmosphere containing an inert gas and a gas containing a hydride of the component of the thin This is because hydrogen termination occurs and high purity is guaranteed. For example, when the thin film includes silicon, the best hydride is silane. silane rapidly reacts, it reacts securely with the unpaired bonding electrons which appear on the surface. This occurs because, as a result of reaction, even if silane is captured by the silicon thin film, only a

silicon atomic layer is formed, without causing either decrease in purity or lattice distortion.

In order to securely effect hydrogen termination in melt crystallization, the partial pressure of hydrogen or hydride in the atmosphere should be about 10 mTorr or more. This is based on the following reasons. If the mass of one molecule of a gas is m (kg), the partial pressure is P (Pa), the temperature is T (K), the concentration is C ( $m^{-3}$ ) and the average velocity is v ( $m \cdot s^{-1}$ ), then the flux density F ( $m^{-2} \cdot s^{-1}$ ) of the gas is represented by the following equation:

$$F = \frac{1}{6}CV = \frac{1}{\sqrt{3kTm}} \qquad \dots \quad (1) \quad [Equation 1]$$

wherein k is the Boltzmann's constant. If the melting time of recrytallization is indicated by  $\tau$  (s), and the density of unpaired bonding electrons on the thin film surface is indicated by Nss (m<sup>-2</sup>), in order to terminate all unpaired bonding electrons, it is a necessary condition that the number of gas molecules (flux density x melting time) which collide with the thin film surface within the melting time is larger than the density of unpaired bonding electrons. Namely, the following equation is established:

 $\tau$  F > Nss ... (2) [Equation 2] From Equations (1) and (2), the following equation is obtained for pressure:

$$\int_{\mathcal{B}^2} \frac{2\sqrt{3kTM}}{\tau} Nss \qquad \dots (3) \quad [Equation 3]$$

When the partial pressure of hydrogen atoms or hydride satisfies Equation 3, a high quality surface can be obtained after melt crystallization. The shortest possible time of melt crystallization is generally 10 ns  $(\tau = 1 \times 10^{-8} \text{ s})$ , and the maximum density of the unpaired bonding electrons, is about  $1 \times 10^{12} \text{ cm}^{-2}$  (Nss =  $1 \times 10^{16} \text{ m}^{-2}$ ). Therefore, if the partial pressure of hydrogen

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molecules or hydride is higher than the pressure calculated using these values, Equation (3) is satisfied in melt crystallization of all thin films. The minimum partial pressure calculated for each hydride is as follows:

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hydrogen molecule ( $H_2$ ) PH $_2$  > 1 mTorr hydrofluoric acid (HF) PHF > 3 m Torr hydrochloric acid (HCl) PHCl > 4 mTorr hydrochloric acid (HCl) PHCl > 4 mTorr silane (SiH $_4$ ) PSiH $_4$  > 4 mTorr nitric acid (HNO $_3$ ) PHNO $_3$  > 6 mTorr sulfuric acid ( $H_2$ SO $_4$ ) PH $_2$ SO $_4$  > 7 mTorr

Equation (3) indicates that the minimum partial pressure of a hydride increases as the molecular weight increases. However, the above results also indicate that almost all materials have a partial pressure higher than The limit about 10 mTorr. lower of hydrogen concentration is about 4%, and the partial pressure of hydrogen corresponding to this value is about 30 Torr. From the viewpoint of safety, the other hydrides are preferably used at concentrations of about 1% or less, or partial pressure of about 7.6 Torr or less. margin for safety, the maximum partial pressure is about Torr. Therefore, the partial pressure of crystallization for all hydrides (including hydrogen molecules), which safely achieves the object of the invention is 10 mTorr to 5 Torr.

Although the partial pressure of the hydride used in the second step has been described above, the total pressure is preferably atmospheric pressure or higher. melt crystallization under low pressure course, satisfies the above partial (vacuum) which pressure condition produces the same effect as described above. vacuum system apparatus, the cost However, in a increased, process is complicated. Melt and the crystallization under atmospheric pressure simplifies the apparatus process, thereby significantly and the

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improving productivity. Further, when processing in the second step is carried out under atmospheric pressure or higher, in metal crystallization, it is possible significantly decrease evaporation and scattering of the component elements of the thin films and adhesion of the evaporated and scattered elements in the apparatus, with processing under vacuum (hereinafter "scattering suppression effect"). This is caused by the fact that the melted surface is pressed by the gases which form the atmosphere, and evaporation and scattering are suppressed in proportion to pressure. Since the degree of this effect is determined by the level of total pressure, in principle, even if the pressure of only the is hydrogen molecules or hydride used increased atmospheric pressure without using an inert gas, the same scattering suppression effect as the use of a mixed gas containing a hydride and an inert gas under atmospheric pressure can, of course, be obtained. However, it is very dangerous to handle such hydrides under atmospheric pressure. For this reason (guarantee of safety), a mixed gas containing hydrogen or hydride and an inert gas is As the inert gas, nitrogen is most widely preferable. used and has the advantage, being inexpensive. metal or semiconductor is put into a high-temperature liquid state by supplying high energy, it reacts with nitrogen. However, rare gases have the advantage that they do not under any circumstances react with any thin film materials, even at high temperatures. Materials utilized for thin films such as silicon and aluminum have relatively high atomic weights. Thus, of the rare gases, elements with high atomic weights, such as argon, krypton and xenon, have the larger scattering suppressing effect. Since krypton and xenon are not found in abundance, these elements are expensive. However, argon gas is inexpensive, practical and exhibits a large scattering suppression effect.

A high energy supply apparatus is required in order for the second step to stably progress. In the second step, high energy is supplied to an object material, such as the semiconductor thin film and metallic thin film formed on the substrate in the first step of the invention, to melt and crystallize at least the surface layer and obtain a high-quality crystal.

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# BRIEF DESCRIPTION OF THE DRAWINGS

These and other aspects and advantages of the invention will become apparent from the following detailed description of preferred embodiments when taken in conjunction with the accompanying drawings, in which:

Fig. 1 shows a conventional laser irradiation apparatus;

Fig. 2 shows a high energy supply apparatus according to an embodiment of the invention;

Fig. 3 shows a high energy supply apparatus of the present invention;

Fig. 4 shows a high energy supply apparatus according to an embodiment of the invention;

Fig. 5 shows a high energy supply apparatus of the invention;

Fig. 6 is a chart showing changes in the high energy supplied to an object material with time;

Fig. 7 is a chart showing changes in the high energy supplied to an object material with time;

Figs. 8(A) - (D) are sectional views showing the respective steps for manufacturing a thin film semiconductor device in accordance with an embodiment of the invention;

shows the configuration of a transmission type liquid crystal display device according to the invention;

Figure 10 is a flowchart showing the configuration of an electronic apparatus according to the invention;

AFigure 11 shows a liquid crystal projector utilizing an electronic apparatus according to the invention;

apparatus (personal computer) utilizing the invention; and

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√Figure 13 shows a further example of an electronic apparatus (pager) utilizing the invention.

## DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The high energy supply apparatus is described using light (laser beam) as an example of a form of high energy, with reference to Figure 2. The method of forming a crystalline film, using the thin film formed on the substrate in the first step of the invention as the object material to which high energy is supplied during the second step, will be discussed.

The high energy supply apparatus, shown Figure 2, includes at least a generation source (laser emission source) 202 for generating high energy 207 such as a laser beam, and a supply chamber 201 in which the generated high energy is supplied to an object material (the substrate on which a thin film is formed). supply chamber 201 has a function (setting base) 205 for setting the object material 203 in the supply chamber. The setting base 205 is provided with a movable function so that the high energy 207 can be supplied to a desired position of the object material. In a portion of the wall 209 of the supply chamber 201 is provided an introduction window 206 for introducing high energy 207 into the supply chamber. The introduction window 206 includes a material which absorbs little high energy and molecules. In other words, the transmits few gas introduction window 206 is transparent to high energy 207 and opaque to gas molecules. For example, when the form of high energy 207 is light, the introduction window includes transparent glass such as quartz.

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In the invention, the introduction window 206 is provided at a position where, when high energy supplied to the object material 203 (for example, silicon thin film), the components (in the case of a silicon thin film, silicon atoms) of the object material 203 hardly adhere to the introduction window. example, in the high energy supply apparatus, a portion of the wall of the supply chamber 201 is projected in a direction apart from the object material 203, and the introduction window 206 is provided at the top of the projected portion 210. As a result, the distance L1 between the introduction window 206 and the object material 203 is larger than the shortest distance L2 between the wall 209 and the object material 203. state where the distance between the introduction window 206 and the thin film as the object material is larger than the shortest distance between the wall 209 and the thin film, i.e., in a state wherein the introduction window 206 is provided at a position where the components of the thin film hardly adheres to the introduction window 206 even by supplying high energy 207 to the thin film, the high energy 207 is supplied to the thin film as the object material 203. In Figure 2, the scattering range of the elements evaporated and scattered from the object material 203 as a result of supply of high energy 207 (irradiation of a laser beam) is shown as scattered component.

In the invention, since the introduction window 206 is sufficiently separated from the object material 203, as compared with the scattering range of the object material 203, the components of the object material 203 hardly adhere to the introduction window even if melt crystallization by supplying high energy 207 is repeated. As described above, the introduction window 206 must be transparent to high energy. Since the object material 203 is opaque to high energy, high energy is converted into heat. If the object material 203 adheres to the

introduction window 206, the introduction window becomes opaque and thus does not have the function to fulfil. In the invention, a high energy supply apparatus having excellent stability and productivity is realized.

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crystallized film When а is obtained by irradiating the semiconductor thin film with a laser is particularly important to control Generally, scattering range. the higher the energy supplied to the semiconductor thin film, the easier a good crystallized film is obtained. However, if the supplied energy exceeds a certain upper limit, are explosively semiconductor elements scattered, resulting in the absence of the semiconductor thin film or a decrease in the thickness thereof after supply of This is possibly caused by the fact that high energy. semiconductor film includes a covalently bonded crystal and is hard and has lower thermal conductivity than that of metals. Another possible cause is that since the semiconductor thin film is deposited by the vapor phase deposition process (CVD process) in the first step, the adhesion between the semiconductor film and the substrate or a surface protective film formed on the substrate is low.

In either case, since the upper limit is present, the energy of the laser beam supplied for performing crystallization is set to as a high value as possible which is lower than the upper limit. However, the energy of the laser beam invariably changes, and explosive scattering occurs in a statistical process. Therefore, in order to obtain a good crystalline semiconductor film, the scattering phenomenon cannot necessarily be ignored. From the above situation, it can be concluded that the high energy supply apparatus and the crystallized film forming method of the present invention, in which the scattering range is controlled, are particularly suitable for stably forming a good crystalline semiconductor film

on the substrate or the surface protective film with high productivity.

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In order to decrease the size of the high energy apparatus and facilitate replacement supply the atmosphere in the supply chamber, the unnecessary space in the supply chamber must be eliminated as much as In consideration of setting and removal of the object material 203 and vibration in the operation of the setting base 205, the shortest distance between the wall and the object material 203 is about 2 mm to 40 mm. the other hand, the scattering range of the object material 203 changes with pressure in the supply chamber. For example, the scattering range under a vacuum of about  $10^{-5}$  Torr reaches approximately 10 cm or more, while the range under atmospheric scattering pressure less. Therefore, melt approximately 10 mm if or crystallization is progressed under pressure of atmospheric pressure or higher, as described above, the sufficient distance between the introduction window 206 and the object material 203 is about 20 mm or more. high energy 207 is supplied under pressure of about 10 mTorr or less, the distance is preferably at least about and ideally 100 mm or more. From mm, viewpoints, in order to comply with various pressures in the supply chamber 201, the distance is preferably about 50 mm or more. Although there is no upper limit of this distance, if the upper limit is positively set, the upper limit is about 1000 mm. If the distance is too long, the volume of the supply chamber is increased, a lot of time is required for replacing the atmosphere, and the size of the apparatus itself is also increased.

The optimum form of the high energy supply apparatus is described above. The gas flow in the supply chamber of the high energy supply apparatus will be  $Figs. \ 3(A) \ and \ 3(B)$  described with reference to Figure 3.

Fig. 3(A) shows the structure of the supply chamber of the high energy supply apparatus described  $\frac{1}{2}\pi$ 

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Athe previous chapter from the viewpoint of the gas flows, shows gas flows 320 in the middle of and Fig. 3(B) crystallization of the object material performed by at least supplying high energy to the object material (the thin film formed on the substrate). The high energy supply apparatus of the invention includes regulating means for generating a desired pressure distribution in the supply chamber 301, or gas flow regulating means for generating desired gas flows in the supply chamber 301. Specifically, referring to Figure 3(A), the pressure regulating means or the gas flow regulating means includes at least an exhaust port 311 and a gas inflow port 312. The exhaust port is provided at a portion of the wall 309 of the supply chamber, for exhausting the air in the supply chamber. A plurality of gas inflow ports (at the 6 positions shown in Fig. 3(A)) are provided for flowing the various gases described in detail earlier in the supply chamber. The amount of the gas flowing through each of the gas inflow ports and the the exhaust rate of port are appropriately adjusted to control the total pressure and flows in the supply chamber by the pressure regulating means and the gas flow regulating means.

Additionally, the pressure regulating means and the gas flow regulating means are capable of increasing the pressure in the vicinity of the introduction window 306 to a value higher than that in the vicinity of the object material, and increasing the pressure in the vicinity of the object material to a value higher than that in the vicinity of the exhaust port. Therefore, in the second step, the high energy 307 is supplied to the object material 303 such as the thin film set on the setting base 305 in the state wherein the pressure in the vicinity of the introduction window is higher than that in the vicinity of the object material 303, or the pressure in the vicinity of the introduction window 306 is higher than that in the vicinity of the object

material 303 (thin film) and the pressure in the vicinity of the object material (thin film) is higher than that in the vicinity of the exhaust port.

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The gas flows in this state will be described with reference to Fig. 3(B). First, the path of the high energy which is introduced into the supply chamber 301 through the introduction window 306 and then applied to the object material 303 is assumed in the supply chamber. Part of the high energy which reaches the object material through the irradiation passage enters the material, and another part thereof is scattered and reflected from the object material. In this application, at Figure 3(A) the scattered reflected high energy is referred to as "reflected energy" 313. The path of the reflected energy 313 in the supply chamber is assumed as a reflection passage 314 as shown in Figure 3B). described above, the pressure distribution and gas flows 320 regulated by the pressure regulating means and the gas flow regulating means, respectively, are present in the supply chamber 301.

In the supply chamber 301 of the high energy supply apparatus of the invention, the gas flows 320 can be controlled so that gases flow toward the material from the introduction window in substantially the same direction as the irradiation passage 315, and flow from the object material in substantially the same direction as the reflection passage 314. This occurs because the pressure in the vicinity of the introduction window 317 is higher than that in the vicinity 318 of the object material 318, and the pressure in the vicinity of the object material is higher than that in the vicinity of the exhaust port 319. Eventually, high energy is supplied to the object material such as the thin film to progress melt crystallization in the state wherein the gases flow from the introduction window in substantially the same direction as the irradiation passage and flow

from the object material in substantially the same direction as the reflection passage.

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As described above, in melt crystallization of a metal or semiconductor, the component elements of the metal or semiconductor are invariably evaporated. With supply of high energy, the component elements scattered as a fine powder. In the high energy supply apparatus of the invention, since gas flow from the introduction window side to the object side is present, the probability that the evaporated elements or scattered the introduction fine powder reach window is significantly decreased. Since gas flow 320 from the object material to the exhaust port is present substantially the same direction as the reflection passage, the evaporated elements or scattered fine powder This fact not only are exhausted through the gas flow. prevents adhesion to and contamination of the supply chamber but also significantly restricts re-adhesion of the evaporated elements or scattered fine powder to the object material.

This, particularly, has an important meaning when a TFT or a super integrated circuit (LSI) is manufactured by using crystallized thin film formed on the substrate. This is because the fine powder which re-adheres to the thin film causes deterioration of precision processing and results in electrical short circuits. Since the fine powder is chemically active and has high reactivity to the wall of the supply chamber, the fine powder possibly re-adheres to the object material such as the thin film after such chemical reaction, thereby deteriorating the purity of the thin film itself. The high energy supply apparatus and the crystalline film forming method of the invention can completely remove these adverse effects, and stably produce a good crystal.

The high energy supply apparatus of the invention described above is further described as a method of forming a crystalline film using the apparatus.

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Fig. 4 shows the structure of a supply chamber 401 of the high energy supply apparatus of the invention. The high energy supply apparatus includes at least a generation source for generating high energy 407 and a supply chamber 401 for supplying high energy 407 to an material 403 (a metallic thin film semiconductor thin film). In the supply chamber, provided setting means 405 having the function to set the object material 403 in the chamber 401. The object material 403, such as a substrate having a thin film formed in the first step of the invention, is set on the setting means. In a portion of the wall 409 of the supply chamber 401, an introduction window is provided for introducing high energy 407 into the supply chamber so that the positional relationship between introduction window 406 and the object material 403 satisfies the conditions described above. In the supply chamber 401 pressure regulating means and gas regulating means, are provided which include an exhaust port 411 and gas inflow ports 312, respectively, so that the pressure distribution and gas flows described earlier are present in the supply chamber 401. Of course, the atmosphere in the supply chamber 401 is set according to the description discussed earlier. The path of the high energy 407 introduced into the supply chamber 401 through the introduction window 406 and then applied to object material 403 the irradiation passage 415.

Ιn the high energy supply apparatus of invention, the introduction window 406 or the setting means 405 is disposed so that the direction, the normal line 416 of the object material 403 such as the thin film shifted from the direction of the irradiation Therefore, in crystallization of the thin passage 415. film, high energy 407 is supplied to the thin film in the state wherein the normal direction 416 of the normal line of the thin film is deviated from the direction of the In the high energy supply irradiation passage 415.

apparatus of the invention, an exhaust port 411 is also the normal direction 416 of provided in the object material such as the thin film. Such a configuration increase in the distance permits between an introduction window 406 and the object material 403 in the small supply chamber 401, and easily produces the same construction and effect described earlier. addition, since the exhaust port 411 is provided at a position at the shortest distance between the object material 403 and the wall of the supply chamber 401, the evaporated elements and scattered fine powder effectively discharged. Further, since the rate of discharge of the evaporated elements and scattered fine powder in the normal direction 416 of the normal line is efficiency of particularly high, the discharge improved, and the effect described in earlier is securely attained.

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The high energy supply apparatus of the invention also includes means for changing the course of reflected energy so that the object material 403 is irradiated again with the reflected energy 413. The course changing means 418 further includes positioning means for permitting a desired position of the object material 403 such as the thin film to be irradiated with the reflected energy 413.

After the thin film formed on the substrate in the first step is set in the supply chamber 401, a first thin film is irradiated with position of the Part of the high energy 407 enters the thin energy 407. film, and another part is reflected from the thin film to generate reflected energy. The course of the reflected energy 413 is changed by the course changing means so that a second position of the thin film is irradiated to progress melt crystallization. If the high energy 407 has a high velocity, as light, irradiation of the second position is generally started with reflected energy corresponding to the high energy for

irradiating the first position of the thin film during the time of irradiation of the first position of the thin film with the high energy. The first position and the position are adjusted second by the positioning means 417. If the high energy 407 is light, the course includes an optical device such as changing means mirror, a lens or a prism. If the high energy is charged course changing particles, the means comprises electromagnetic generator. The positioning function 417 is the function to change the positional relation (for example, the angle of the mirror) of an optical device, or finely adjust an electromagnetic field.

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AFigure 5 shows the simplest apparatus using light as high energy where 506 is an introduction window, 511 is an exhaust port, 512 is a gas inflow port and 516 is a line. Course changing means normal 518 includes mirror, preferably converging means such as a concave mirror. Although reflected light generally contains scattered components, the converging means converges efficient scattered light to permit re-irradiation. Incident light is applied to the object material 503 such as the thin film and is then partially reflected to generate reflected light 513. The reflected light 513 is converged and reflected by the concave mirror, and then applied to the object material 503 again. This can significantly increase the efficiency of utilization of high energy 507. For example, reflectance ultraviolet light and visible light by a semiconductor thin film reaches about 70% or more, and the reflectance by a metal thin film is about 90% or more. Although a conventional efficiency of energy utilization approximately 10% to 30%, the invention can substantially double the efficiency of energy utilization approximately 20% to 50% because the reflected energy 513 efficiency re-utilized. This is particularly remarkable when the irradiation position (first position) where the object material is irradiated with high energy is substantially the same as the irradiation position (second position) where the object material is irradiated with the reflected energy.

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This effect is described with reference to an example in which a laser beam is emitted as pulses and is illustrated in Figure 6. In Fig. 6, the time at the nonirradiation point of the object material is shown on the abscissa, and irradiation is started at t = 0. energy (arbitrary unit) which intensity of the object material to contribute to crystallization is shown on the ordinate axis. When irradiation is started, the energy intensity of the high energy is increased to the maximum at  $t = t_1$ . reflected energy is applied to the object material with a slight delay corresponding to the distance between the object material and the course changing means and the It is assumed that the time the energy density of the reflected energy is the maximum is  $t_2$ , the delay is indicated by  $t_2 - t_1$ . In this way, the energy density of the incident high energy is superimposed on the energy This total of energy density of the reflected energy. density actually contributes to melt crystallization. shows this effect as synthetic light. described above, the invention can substantially double the conventional efficiency of energy utilization.

In the high energy supply apparatus of the invention, the course changing means has the function of adjusting time. This function delays the time (shown by t2 - t1 in Fig. 6) of re-irradiation of the object material with the reflected energy (hereinafter "the delay time"). For example, the time regulating means 419 in Figure 4 can be composed of a plurality of reflecting means which can reflect the high energy. Figure 4 shows a simple example of this means. If the high energy is light, the reflecting means is composed of combination of mirrors. The time regulating means 419 is means for changing the length of the course of the reflected energy

413 or changing the velocity of the reflected energy 413. The former means is useful when the high energy is light, and the latter means is useful when the high energy is charged particles. This is because the course length of light can be changed by changing combination of mirrors, and the velocity of charged particles can be changed by adjusting an electric field. The irradiation time of the object material with high energy can be increased by appropriately adjusting the delay time. This will be described below with reference to Figure 7.

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described below with reference to Figure 7.

In Fig. 7, the same things as those shown in Fig. 6 are respectively shown on the abscissa and the ordinate. In Fig. 7, the delay time  $(t_2 - t_1)$  is substantially the same as the emission time width (the half width of incident light shown by  $t_a$  in Fig. 7) of the high energy. As a result, the half width of the synthetic light is substantially doubled (shown by  $t_b$  in Fig. 7).

An increase in the time half width of the high energy means that energy is rapidly supplied to the object material, and the probability of occurrence of the explosive scattering can significantly be decreased. example, the hydrogenated amorphous silicon film (a-Si:H) by a plasma chemical vapor phase deposition process (PECVD process) is used as the object material, and the object material is crystallized by irradiation with a xenon chlorine (XeCl) excimer laser (abbreviated to a XeCl laser with a wavelength of 308 nm) This thin film generally has a high hydrogen content and a low density, and is thus very difficult to In fact, an amorphous film is not at melt crystallize. all crystallized by a XeCl laser having a time half width of about 50 ns with an irradiation energy density of about 100 mJ·cm<sup>-2</sup> or less. Conversely, if the energy density exceeds this value, explosive scattering occurs. Eventually, the thin film is not crystallized over the entire energy region. On the other hand, the amorphous

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thin film is not crystallized by a XeCl laser having a time half width of about 100 ns with an irradiation energy density of about 100 mJ·cm<sup>-2</sup> or less, while with an energy density between about 100 mJ·cm<sup>-2</sup> to 150 mJ·cm<sup>-2</sup>, melt crystallization completely proceeds. Although, with an energy density of about 150 mJ·cm<sup>-2</sup> or more, explosive scattering occurs as described above, energy density range which enables melt crystallization is widened by further increasing the time half width. Even with the same energy density of 125 passage. Thisis caused mJ·cm<sup>-2</sup>, high energy having a short time half width (50 ns) and high energy having a long time half width (100 ns) have different effects on the object This difference is based on a difference in the energy transfer per unit time. With a long time half width, the amount of the energy transferred from high energy to the object material per unit time is decreased, thereby suppressing the explosive scattering. This is the same as a difference between combustion and explosion of an explosive. Explosion means the phenomenon which occurs when the energy transfer per unit time is large. reasons. in melt crystallization these amorphous semiconductor film formed by PECVD or sputtering process at a relative low temperature (the substrate temperature is about 400°C or less) by supplying high energy, the time half width of the high energy is preferably about 100 ns or more. As described above, it is possible to simply increase the time half width, and crystallize the thin film which was conventionally considered as difficult to melt crystallize.

The high energy supply apparatus described in detail above, and the crystalline film formed by using the apparatus can be applied to various thin film electronic devices, including semiconductor devices such as TFTs and LSIs, metal-insulator-metal elements (MIM elements), solar cells, printed boards, etc., and the performance can significantly be improved. A method of

manufacturing an excellent thin film electronic device with reference to a TFT with highest applicability as an example is described.

AFigures 8(A) - (D) are schematic sectional views showing the steps of manufacturing a thin film semiconductor device (so-called TFT) which constitutes a MIS type field effect transistor. The method of manufacturing a TFT in accordance with the invention will be briefly described.

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The invention uses general purpose non-alkali glass as a sample substrate. In Afigure 8(A), substrate 801 is formed a surface protective film 802 including an insulator by an atmospheric pressure chemical vapor deposition process (APCVD process), PECVD process or a sputtering process or the like. semiconductor film, such as an intrinsic silicon film serving as an active layer of a thin film semiconductor device, is then deposited as the first step for the semiconductor film. The semiconductor film is formed by a chemical vapor deposition process (CVD process) such as APCVD or LPCVD or a physical vapor deposition process (PVD process) such as sputtering or vapor deposition. The semiconductor film is supplied with high energy, such as a laser beam for example, to progress melt crystallization second step for the semiconductor film. If the thin film deposited in the first step is amorphous or a mixed crystal containing an amorphous material and a fine crystal, this second step is generally called "the crystallization step" other hand, if the thin film deposited in the first step polycrystalline, the second step is called No distinction is made between recrystallization step. cases, and this step is simply called both "crystallization step." Both cases correspond to the melt crystallization of this application as long as at least the surface of the thin film is melt crystallized by supplying high energy.

Melt crystallization is an excellent technique from the viewpoint that a high quality crystalline thin film can be formed on a large substrate with high productivity. In melt crystallization, by supplying high energy, the energy supply time (with a laser beam, the irradiation time) is generally as short as about 10 ns to 500 ns, and the energy supply region (laser irradiation region) is localized on the entire substrate. Thus, in crystallization, entire substrate is the not simultaneously heated to a high temperature, thereby causing no deformation and crack due to the heat of the After the crystalline semiconductor film substrate. (polycrystalline silicon film) is formed according to the crystalline film forming method described above, the crystalline semiconductor film is processed to an island form, and an active semiconductor film 803 serving as an active layer of a transistor is formed.

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After the active semiconductor film is formed, a gate insulating film 804 is formed by CVD or PVD Fig. (Fig. 8(b)) as illustrated in Figure 8(B).

Referring to Figure 8(C), a metallic thin film serving as a gate electrode 805 is then deposited by PVD Since the gate electrode and gate wiring are or CVD. generally formed by using the same material in the same step, the material used must have low electric resistance and resist the highest temperature (in this example, about 350°C) and chemicals in the subsequent steps for manufacturing the thin film electronic device. tantalum (Ta) film having such properties is formed by sputtering. The tantalum thin film formed by sputtering generally has a  $\beta$ -structure and resistivity of as high as about 200  $\mu\Omega$ cm. The tantalum thin film also has internal stress and is apt to cause disconnection when used for In the invention, therefore, high energy is wiring. supplied to the tantalum thin film (a second step for the metal) to improve the quality of the thin film. melt crystallization of the tantalum metallic thin film is progressed by the method described earlier, the crystallized film comprises  $\alpha$ -structure tantalum (Ta). The  $\alpha$ -structure tantalum has a cubic crystal system and a body-centered cubic crystal structure (bcc). The  $\alpha$ -structure tantalum also has a resistivity of about 20  $\mu\Omega$ cm to about 60  $\mu\Omega$ cm and low internal stress. The  $\alpha$ -structure tantalum is an excellent wiring material as compared with the above  $\beta$ -structure tantalum.

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After the metallic thin film, which serves as the gate electrode and gate wiring is formed, shaping is carried out. Then, impurity ions are injected into the active semiconductor film to source-drain regions and a channel formation region 806, 807 and 808, as illustrated At this time, since the gate electrode in Figure 8(C). is used as a mask for ion injection, the channel formation region is formed only under the gate electrode in a self alignment manner. In order to inject impurity ions, two methods can be used: an ion doping method for impurity elements injecting hydride and hydrogen as injected by using a mass non-separation ion injection apparatus; and an ion implantation method for injecting desired impurity element only by using separation type ion injection apparatus. When a CMOS TFT appropriate formed, mask material, is an such as polyimide resin, is used and NMOS and **PMOS** alternately masked to inject each ion by using one of the methods described above.

Referring to Figure 8(D), a layer insulating film 809 is then formed by CVD or PVD. After ion injection and formation of the layer insulating film, heat treatment is carried out for between several minutes to several hours in an appropriate heat environment of about 350°C to activate the injected ions and thermally shrink the layer insulating film. After the layer insulating film is formed, contact holes are formed above the source and drain, and a source-drain lead-out electrode 810 and

811 are formed. Αt this time, the the metallic crystallization of thin film described earlier may be applied to the metal which constitute the source-drain electrodes and wiring, as the gate electrode and gate wiring. After the crystalline metallic film is formed, the thin film is processed to electrodes and wiring to complete a thin film semiconductor device (Fig. 8(d)).

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The substrate and the surface protective film is described below. Substrate materials to which the invention can be applied include conductive materials such as metals, ceramic materials such as silicon carbide (SiC), alumina (Al<sub>2</sub>O<sub>3</sub>), and aluminum nitride transparent insulating materials, such as fused quartz, glass; semiconductor substrates including silicon wafers; crystalline insulating materials, such LSI obtained by processing semiconductor substrates, and sapphire (trigonal system Al<sub>2</sub>O<sub>3</sub> crystal).

As an example of inexpensive general purpose glass substrate, #7059 glass or #1737 glass produced by Corning Japan Co., Ltd. or OA-2 glass produced by Nippon Denki Glass Co., ltd., NA35 glass produced by NH Technoglass Co., Ltd. can be used.

semiconductor device а thin film manufactured by using a crystalline semiconductor thin film, or when metallic wiring is formed by using a crystalline metallic thin film, at least a part of the substrate comprises an insulating material, and crystalline thin film is formed on the insulating material regardless of the type of the substrate used. The insulating material film is hereinafter referred to as "the surface protective film". For example, when a fused quartz substrate is used, since the substrate itself includes an insulating material, a crystalline film may be formed directly on the fused Alternatively, the crystalline thin film may substrate. be formed after an insulating material such as a silicon .

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oxide film (SiO<sub>x</sub>: O < x  $\leq$  2) or a silicon nitride film (Si<sub>3</sub>N<sub>x</sub>: O < x  $\leq$  4) is formed as the surface protective film on the fused quartz substrate.

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When a glass plate is used as the substrate, generally, a crystalline film such as a semiconductor film may be formed directly on the glass substrate including an insulating material. However, in order to prevent contamination of the thin film with movable ions such as sodium (Na) contained in glass, the crystalline film is preferably formed after the surface protective film is formed on the glass substrate by using insulating material such as silicon oxide or silicon The thin film electronic device, such as the nitride. thin film semiconductor device manufactured as described earlier, has no variation in operational characteristics in use for a long time or under a high voltage, thereby improving stability. In the case of the crystalline semiconductor film, the thin film is preferably formed on the surface protective film, except the case where a crystalline insulating material such as sapphire is used When any one of various ceramic as the substrate. is used as the substrate, the substrates protective film is preferably provided for preventing a sintering auxiliary material added to ceramic diffusing into the thin film and contaminating it. a metallic material is used as the substrate, the surface protective film is necessary and essential to secure insulating properties. In addition, in a semiconductor substrate and LSI device, the layer insulating film or the like provided between transistors or wiring layers plays a part as the surface protective film. and shape of the substrate are not at all limited as long as no deformation such as shrinkage, distortion or the like occurs in the heat environment of the manufacturing process. Namely, any desired substrate including a disk having a diameter of 3 inches (76.2 mm) and a rectangular substrate of about 600 mm x 800 mm or more can be used.

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The types of semiconductor films to which the invention can be applied include single semiconductor films of silicon (Si), germanium (Ge) semiconductor films element composite materials of Group ΙV such silicon germanium ( $Si_xGe_{1-x}$ : 0 < x < 1), silicon carbide  $(Si_xC_{1-x}: 0 < x < 1)$ , germanium carbide  $(Ge_xC_{1-x}: 0 < x < 1)$ 1); semiconductor thin films of composite compounds of Group III elements and Group V elements such as gallium arsenic (GaAs), indium antimony (InSb); and thin films of composite compounds of Group II elements and Group VI elements such as cadmium selenium (CdSe). The invention can also be applied to semiconductor thin films composite compounds such as silicon germanium gallium + arsenic (SixGeyGazAsz: x + У Z = 1), semiconductor films obtained by adding a donor element such as phosphorus (P), or arsenic (As), antimony (Sb) to the semiconductor films; and P-type semiconductor films obtained by adding an acceptor element such as boron (B), aluminum (Al), gallium (Ga), indium (In) the semiconductor films.

When the semiconductor film includes silicon gases containing the component element of the semiconductor film include silanes, such as monosilane disilane  $(Si_2H_6)$ , trisilane  $(Si_3H_8)$ ,  $(SiH_4)$ , dichlorosilane (SiH<sub>2</sub>Cl<sub>2</sub>). When the semiconductor film includes germanium, germane (GeH4) is used. semiconductor film includes phosphorus (P) or boron (B), or when such an element is added to an intrinsic semiconductor film, phosphine (PH<sub>3</sub>), diborane (B<sub>2</sub>H<sub>6</sub>) can also be used. Although chemical materials containing the elements which include the above various semiconductor films are used as gases for forming the atmosphere, because these gases partially remain in the semiconductor films, hydrides of the component elements are preferably For example, chlorine (Cl) remains in a silicon used. film formed by using dichlorosilane (SiH2Cl2) regardless of the amount of chlorine, and thus residual chlorine

causes deterioration in transistor characteristics when the silicon film is used for the active layer of a thin film semiconductor device. Therefore, monosilane ( $SiH_4$ ) which is a hydride of the component element, is preferred as compared with dichlorisilane.

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Types of light sources, when a laser beam is used as high energy is described below. The laser beam used in the invention is not limited, and various sources are used in accordance with the object material used. A KrF excimer laser (wavelength 248 nm) and a XeCl excimer laser (wavelength 308 nm) are widely used in the industrial field because of stable emission of light. excimer laser and a XeF excimer Also, a ArF (wavelength 351 nm) can also be used as the excimer A YAG laser, a carbon dioxide laser, a Ar main beam laser (wavelength 514.5 nm), a Ar sub-beam laser (wavelength 448 nm), a HeNe laser (wavelength 632.8 nm), a HeCd laser (wavelength 441.6 nm), and other various pigment lasers can also be used. When the material is a semiconductor film which includes silicon as a main component, a XeF laser, an Ar main beam laser, Ar sub-beam laser, HeNe laser, and HeCd laser exhibit higher absorption coefficients in the amorphous component than that in the crystalline component. This means that in a system containing an amorphous component and a crystalline component, energy absorption of the amorphous higher than that of the crystalline component is component, and the temperature of the amorphous component Namely, crystallization of the amorphous easily rises. component more easily takes place than recrystallization of the crystalline component.

As described above, in melt crystallization of the semiconductor film, as the energy supplied increases which damage within the range causes no the semiconductor film, the quality of the crystallized film Ιf temperature obtained is improved. the the crystalline easily component more rises, the

semiconductor film is damaged before the component is completely crystallized. In other words, damaged before recrystallization the film is The XeF laser, for example, does not cause completed. damage to the film, and is therefore very suitable for melt crystallization of a silicon semiconductor film. is therefore important to select a high energy source whereby the absorption coefficient of the object material before supply of high energy is higher than that of the crystalline object material after supply of high energy.

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Since the KrF laser and XeC laser exhibit high absorption coefficients in a semiconductor film including silicon as a main component, these lasers are suitable for crystallization of thin films having a thickness of approximatley 50 nm or less. The absorption coefficients of the XeF laser and HeCd laser are slightly lower than those of the KrF laser and XeCl laser, and thus the XeF laser and HeCd laser are suitable for crystallizing silicon semiconductor thin films having a thickness of about 50 nm to 1000 nm. Since the absorption coefficients of Ar main beam laser and Ar sub-beam layer laser and HeNe laser in semiconductor films are low, they are crystallizing semiconductor suitable for thin having a thickness of about 1000 nm or more.

As described above, the invention enables simple stable melt crystallization of the object material by supplying high energy thereto and easy formation of high-quality crystalline films. Such crystalline thin films permit manufacture of excellent thin film electronic devices. Specifically, the invention has the following effects:

(1) Since crystallization progresses under control of an atmosphere which can safely be replaced, no impurity such as oxygen, nitrogen or dust are captured by the crystalline thin film. Particularly, when the crystalline film includes a semiconductor or metal, high purity and high quality crystalline film can be obtained.

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(2) It is possible to supply high energy under atmospheric pressure, and thus simplify the high energy supply apparatus. This decreases the cost of a thin film electronic device which includes the crystalline film, and increases productivity.

- (3) In melt crystallization, the component elements of the object material are necessarily scattered or evaporated from the melted object material. It is possible to protect the incident window from evaporation, and thus keep the high energy supplied to the object material constant. A crystalline film having good characteristics can thus be obtained, and the quality of the film is significantly stabilized.
- (4)As melt crystallization progresses supplying high energy, such as laser irradiation, to the object material and as the energy supplied increases, the quality of the resultant crystal is generally improved. Since high energy can be applied under atmospheric pressure, even if the supplied energy is increased, phenomenon such as scattering or evaporation suppressed, thereby improving the quality of the crystalline film.
  - Control of the surface plays an (5) important in obtaining a good crystalline film. In the crystallization method of the invention, the control of surface is sufficiently achieved, and thus the excellent crystalline film can be obtained. since the recrystallized surface is controlled to the same state for each melt crystallization, the film characteristics are significantly stabilized.
  - (6) The efficiency of use of high energy can be substantially doubled. In addition, the time half width can be increased, and a material which cannot be crystallized by a conventional process can be crystallized.

In another embodiment of the invention, a surface protective film including a silicon oxide film formed on

a large glass substrate of 360 mm x 475 mm x 1.1 mm by the PECVD process, and an intrinsic silicon film is then formed on the surface protective film without breakage of vacuum. This is the first step for silicon deposition. The thickness of the surface protective film is 300 nm, and the thickness of the semiconductor film is 60 nm. The glass substrate in equilibrium with room temperature is set in an PECVD apparatus in which a lower plate electrode is kept at a temperature of 380°C. Conditions for depositing the silicon film are as follows:

Time: t = 164 s

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Flow rate of silane:  $SiH_4 = 100$  SCCM

Flow rate of argon: Ar = 3000 SCCM (raw material concentration 3.23%)

Power of radio frequency:  $RF = 600 \text{ W} (0.228 \text{ W/cm}^2)$ 

Pressure: P = 1.5 Torr

Electrode distance: S = 37.1 mm

Temperature of the under plate electrode: Tsus = 380°C

Temperature of the substrate surface: Tsub = 349°C.

The deposition rate of the semiconductor film under these conditions was 0.365 nm/s, and the thickness of the semiconductor film was 60 nm. The hydrogen concentration of the silicon film which measured by thermal was desorption gas spectroscopy (TDS) was 10.39 atomic %. Observation by а transmission electron microscope indicated that the silicon film mainly includes a mixed structure amorphous crystal containing a prismatic The results of Raman spectroscopic component. measurement of the silicon film show a Raman shift at about 520 cm<sup>-1</sup>, and thus indicates that the silicon film of the invention includes a mixed crystal.

The silicon film was then irradiated with a laser beam to progress melt crystallization, the second step for silicon. Melt crystallization is carried out by a high energy supply apparatus having the laser irradiation

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chamber (supply chamber) shown in Figure 4. The laser beam is irradiated by using a KrF excimer laser having a wavelength of 248 nm and a half width of about 33 ns. Since reflected light is applied again with a delay time by the time regulating means, 30 ns about substantial time half width is about 60 ns. regulating means includes a combination of mirrors, and the total length of the optical path of the reflected Incident light is applied at an light is about 9 m. angle of 60° with respect to the normal line. shortest distance between the thin film and the wall of the supply chamber is 20 nm, the distance between the introduction window and the irradiation position on the thin film is generally 40 nm. The laser beam has a linear shape having a width of 120 µm and a length of The widthwise overlap of the beams applied in respective irradiations is 90% of the width of a beam. Therefore, a beam advances by 12 µm in each irradiation, and the same point on the semiconductor thin film is irradiated with a laser beam ten times. The energy density of the laser beam is 150 mJ·cm<sup>-2</sup>. Irradiation of the laser beam is performed under atmospheric pressure. containing argon and monosilane gases introduced into the supply chamber at a rate of 1 slm through the gas inflow port, and discharged through the exhaust port provided on the normal line of the thin The gases flow from the introduction window and the course changing means, including the positioning function and the time regulating means to the irradiation position, and further continues from the irradiation position toward the exhaust port.

Since the silane concentration of argon is generally 100 ppm, the partial pressure of silane is generally about 76 mTorr in irradiation with the laser beam. In irradiation with the laser beam, the substrate temperature is at room temperature of about 25°C. The degree of crystallization of the crystallized

semiconductor film, which was measured by multiwavelength dispersion type epsometory, was 98%, and the thickness was 55 nm. Raman spectroscopic measurement shows a sharp peak with a half width of 4.4 cm<sup>-1</sup> at about 515 cm<sup>-1</sup> which indicates a Raman shift caused by the crystalline component. This indicates that a high quality film having high crystallinity is formed. After the crystallization step, this crystalline film is patterned, and an active layer semiconductor film serving as an active layer of a transistor is then formed.

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A gate insulating film is then formed by PECVD. The gate insulating film including a silicon oxide film is deposited to a thickness of 100 nm at a substrate surface temperature of 350°C by using TEOS (Si-(O-CH<sub>2</sub>-CH<sub>3</sub>))<sub>4</sub>), oxygen (O<sub>2</sub>) and water (H<sub>2</sub>O) as raw material gases and argon as a dilution gas. After the gate insulating film is formed, the oxide film is heat-treated in an atmosphere containing oxygen at a partial pressure of about 0.2 atm and water vapor with a dew point of about 80°C at a temperature of about 350°C for about 3 hours to improve the quality of the insulating film.

A tantalum (Ta) thin film serving as a gate electrode is then deposited by sputtering (the first step In sputtering, the substrate temperature for tantalum). is 150°C, and the thickness of the film is 500 nm. tantalum film is then irradiated with a laser (the second step for tantalum). Conditions for laser irradiation are the same as the conditions for crystallization of the semiconductor film except that the atmosphere changed to mixed gases containing argon and hydrogen. Since the hydrogen concentration of argon is about 1%, the partial pressure of hydrogen in laser irradiation is generally 7.6 Torr. The tantalum film after laser irradiation has the  $\alpha$  structure, as described earlier, and a resistivity of about 40  $\mu\Omega$ cm. After the tantalum thin film is formed as the gate electrode pattering is performed.

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impurity ion is then injected into the An semiconductor film to form source-drain regions and a channel region. At this time, the gate electrode served as a mask for injection, and the channel is formed only under the gate electrode in the self alignment manner. In this example,  $_{\Lambda}^{\mathcal{D}}$ TFT having a CMOS structure is formed. The PMOS TFT portion is covered with a polyimide resin in formation of NMOS TFT source-drain, and conversely the NMOS TFT portion is covered with a polyimide resin in formation of PMOS TFT source-drain to form the CMOS TFT. impurity ion is injected by using a mass separation type ion injection apparatus, and about 5% of phosphine (PH3) diluted with hydrogen is used as a raw material gas for HMOS. The total of the ions including  $PH^{3+}$  and  $H_2^+$  implanted is 1 x  $10^{16}$  cm<sup>-2</sup>, and the concentration of phosphorus atoms in the source-drain regions is about 3 x  $10^{20}$  cm<sup>-2</sup>. In ion injection, the substrate temperature is 250°C. For PMOS TFT, about 5% of diborane  $(B_2H_6)$  diluted with hydrogen is used as a raw material gas. The total of the ions including  $\mathrm{B_2H_6}^+$  and  ${\rm H_2}^+$  implanted is 1 x  $10^{16}$  cm<sup>-2</sup>, and the concentration of boron atoms in the source-drain regions is about  $3 \times 10^{20}$ cm<sup>-2</sup>. In ion injection, the substrate temperature is also 250°C.

A layer insulating film including a silicon oxide film is then formed by the PECVD process using TEOS. deposition of the layer insulating film, the surface temperature of the substrate is 350°C, and the thickness Then heat treatment is performed of the film is 500 nm. at 350°C in an oxygen atmosphere for 1 hour to activate and thermally shrink injected ions the Contact holes are the formed on the insulating film. and (A1) source-drain, aluminum is deposited sputtering. In sputtering, the substrate temperature is

150°C, and the thickness of the Al film is 500 nm. The aluminum thin film for forming a source-drain lead out electrode and wiring is patterned to complete a thin film semiconductor device.

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The transistor characteristics of the thin film semiconductor device formed on an experimental base were The source-drain current Ids when measured. transistor is turned on at a source-drain voltage Vds of ±4 V and a gate voltage Vgs of ±10 V is defined as an on current ION (+ and - signs of voltage indicate the measurement conditions of NMOS and PMOS, respectively). The source-drain current Ids when the transistor turned off at Vds of  $\pm 4$  V and Vgs of 0 V is defined as an was carried out off current. Measurement transistor in a channel formation region having a length L of 5  $\mu$ m and a width W of 5  $\mu$ m at a temperature of 25°C. Mobility and threshold voltage were calculated from the saturation current. In this embodiment, in order to examine the performance of the transistor and variations in the substrate thereof, measurement was made for 50 transistors uniformly formed on a large glass substrate. The results obtained are as follows:

NMOS TFT

ION =  $(74.3 + 9.0, -6.8) \times 10^{-6} \text{ A}$ 25

IOFF =  $(1.38 + 0.53, -0.37) \times 10^{-12} \text{ A}$   $\mu = 124.1 \pm 12.6 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$ Vth =  $2.13 \pm 0.13 \text{ V}$ PMOS TFT

ION =  $(51.6 + 4.7, -4.1) \times 10^{-6} \text{ A}$ IOFF =  $(3.87 + 0.99, -0.80) \times 10^{-13} \text{ A}$   $\mu = 69.3 \pm 6.04 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$ 

 $Vth = -1.11 \pm 0.11 V$ 

Therefore, the invention is capable of uniformly manufacturing a excellent CMOS thin film semiconductor device with high mobility on a large general-purpose glass substrate at a high temperature (350°C) which is the same temperature as a conventional a-Si TFT. Since the

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TFT obtained in this example includes a good crystalline semiconductor film and gate electrode, its reliability as a transistor is extremely high, and its operation is stable over a long period of time. In a conventional uniformity low-temperature process, of laser crystallization is a very important problem regardless of the substrates and lots. However, the invention can significantly decrease variations in the on-current and This significant improvement in uniformity means that the crystalline silicon film of the invention has excellent properties and crystallization is stably progressed by the laser irradiation apparatus energy supply apparatus) used. In addition, since the tantalum film has low stress and low resistivity, when the thin film semiconductor device of the invention is applied to LCD, uniform image quality can be obtained over the entire LCD screen. Further, when a circuit is formed by using the thin film semiconductor device of the invention, not only simple circuits such as a shift register and an analog switch but also complicated circuits such as a level shifter, a digital converter circuit, a clock generator circuit, γcorrection circuit, and a timing controller circuit can be easily formed.

In another embodiment of the invention, an active thin matrix substrate containing the NMOS film semiconductor device described above and used as a color LCD pixel switching element comprising 200 (line)  $\times$  320 (column) x 3 (color) = 192000 (pixels), the CMOS thin film semiconductor device obtained as described above and used as a 6-bit digital data driver (column measurement driver) and a scanning driver (line measurement driver) was manufactured. The digital driver of this embodiment includes a clock signal line, a clock generator circuit, a shift register circuit, a NOR gate, a digital image signal line, a latch circuit 1, a latch pulse line, a latch circuit 2, a reset line 1, an AND gate, a standard

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potential line, a reset line 2, a 6-bit D/A converter based on volume division, a CMOS analog switch , a common potential line, and a source line reset transistor, the output from the CMOS analog switch being connected to the source line of the pixel portion. The volume of the D/A converter satisfies the relation of  $C_0 = C_1/2 = C_2/4 = C_3/8$  $= C_4/16 = C_5/32.$ The digital image signal line directly input to the digital image signal output from a video random access memory (VRAM) of a computer. pixel portion of the active matrix substrate of this embodiment, the source electrode and source wiring, drain electrode (pixel electrode) includes aluminum to form a reflection type LCD. A liquid crystal panel including active matrix substrate as one of a pair substrates is manufactured. A polymer dispersion liquid crystal (PDLC) in which a black pigment is dispersed is used as a liquid crystal held between the pair substrates to form a reflection type liquid crystal panel in a normally black mode (a black display when no voltage is applied to the liquid crystal). The liquid crystal panel is connected to external wiring to produce a liquid crystal display device. As a result, the NMOS and PMOS have substantially the same <del>on</del> resistance and transistor capacity, TFT has high performance, and the parasitic capacity of the transistor is very low. Further, since characteristics are uniform over the entire surface of the substrates, the 6-bit digital data driver and the scanning driver are normally operated over wide Since the pixel portion has a high operation range. degree of opening, even if black pigment dispersion PDLC is used, a high quality liquid crystal display device can be obtained. Further, since the manufacturing process of the active matrix substrate is stable, the liquid crystal display device can stably manufactured at low cost.

This liquid crystal display device is contained in a casing of a full-color portable personal computer. The active matrix substrate contains the 6-bit digital

data driver, and a digital video signal is input directly into the liquid crystal display device form the computer, the circuit configuration is simplified, and at the same is significantly power consumption decreased. time. Since the liquid crystal thin film semiconductor device is a good electronic has high performance, the PC apparatus having a clear display screen. In addition, on the basis of the fact that the liquid crystal display device is a reflection type having a high degree of light is made unnecessary, opening, a back realizing decreases in the size and weight of a battery and long-term use. As a result, a very small lightweight electronic apparatus which can be used for a long time and which has a beauty display screen could be formed.

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Although an example using the reflection type active matrix substrate had been described above, an embodiment of the invention can be applied to a liquid crystal display device including a transmission type active matrix substrate. Figure 9 shows the entire configuration of an example of such a liquid crystal display device. Namely, a liquid crystal display device includes a back light 900, a polarizing plate 901, an active matrix substrate 903 provided with a driving circuit 902, a liquid crystal 904, a counter substrate 905 and a polarizing plate 906.

illustrated in Figure 10, an electronic As apparatus including the liquid crystal display device of this embodiment includes a display information output source 1000, a display information processing circuit 1002, a display driving circuit 1004, a display panel 1006 such as a liquid crystal panel, a clock generator and a power source circuit 1010. circuit 1008 display information output source 1000 includes memory such as ROM and RAM, and a tuning circuit for tuning a television signal and outputting it so as to output display information such as a video signal on the basis of the clock generated from the clock generator circuit outputs display information processing circuit 1002 outputs display information on the basis of the clock generated from the clock generator circuit 1008. The display information processing circuit 1002 includes, for example, an amplification-polarity inversion circuit, a phase development circuit, a rotation circuit, a gamma correction circuit or clamp circuit. The display driving circuit 1004 comprises a scanning-side driving circuit and a data-side driving circuit to drive the liquid crystal panel 1006 to display an image. The power source circuit 1010 supplies electric power to each of the above circuits.

Examples of electronic apparatus having the above-described configuration include the liquid crystal projector, shown in Figure 11, a personal computer (PC) for multimedia and an engineering work station (EWS) shown in Figure 12, the pager shown in Figure 13, a portable telephone, a word processor, a television, a view finder type or monitor direct-viewing type video tape recorder, an electronic notebook, a table electronic computer, a car navigation device, POS terminal, and a device with a touch panel.

The liquid crystal projector shown in Figure 11 is a projection type projector which includes a transmission type liquid crystal panel as a light valve, for example, employs a three-plate prism optical system.

In the projector 1100 shown in Figure 21, the projection light emitted from a white light source lamp unit 1102 is divided into the three primary colors R, G and B by a plurality of mirrors 1106 and two dichroic mirrors 1108 in a light guide 1104, and the three light parts are guided to three liquid crystal panels 1110R; 1110G and 1110B for respectively displaying images of the three colors. The light parts modulated by the liquid crystal panels 1110R, 1110G and 1110B are respectively incident on the dichroic prism 1112 in three directions. In the dichroic prism 1112, red light R and blue light B

are bent at 90°, and green light straight travels to form an image of each color. As a result, a color image is projected on a screen through a projection lens 1114.

The personal computer 12000 shown in Figure 12 includes a body part 1204 having a key board 1202, and a liquid crystal display screen 1206.

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The pager shown 1300 in Figure 13 includes a liquid crystal display substrate 1304, a liquid guide 1306 with a back light 1306a, a circuit substrate 1308, first and second shield plates 1310 and 1312, two elastic conductors 1313 and 1316, and a film carrier tape 1318, all of which are provided in a metallic frame. The two elastic conductors 1314 and 1316 and the film carrier tape 1318 are adapted for connecting the liquid crystal display substrate 1304 and the circuit substrate 1308.

In this apparatus, the liquid crystal display substrate 1304 includes a liquid crystal held between two transparent substrates 1304a and 1304b to form at least a dot matrix type liquid crystal display panel. On one of the transparent substrates can be formed the driving circuit 1004 shown in Figure 10 or the driving circuit 1004 and the display information processing circuit 1002. Circuits which are not provided on the liquid crystal display substrate 1304 can be provided as external circuits of the liquid crystal display substrate on the circuit substrate 1308 shown in Figure 13.

igure 13 shows the configuration of the pager, and thus the circuit substrate 1308 other then the liquid crystal display substrate 1304 is required. However, when a liquid crystal display device is used as a component of an electronic apparatus and when a display driving circuit is mounted on a transparent substrate, the minimum unit of the liquid crystal display device is liquid crystal display substrate 1304. the Alternatively, the liquid crystal display substrate 1304 fixed to the metallic frame 1302 serving as a casing can also be used as a liquid crystal display device as a component of an electronic apparatus. Further, in the case of a back light type, the liquid crystal display substrate 1304 and the light guide 1306 provided with the back light 1306a can be contained in the metallic frame 1302 to form a liquid crystal display device.

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The high energy supply apparatus of the invention capable of stably producing high-guality crystallized films. The crystalline films can be applied film electronic apparatus such as thin semiconductor devices, and significantly improve performance thereof. The invention can thus produce a thin film semiconductor device with high performance by using a low temperature process in which, for example, a low-price glass substrate can be used. invention is applied to manufacture of an active matrix high quality large liquid crystal display device, a liquid crystal display device can easily and stably be manufactured. Further, when the invention is applied to manufacture of an electronic circuit, a high quality electronic circuit can easily stably be manufactured.

The invention is not limited to the above embodiments, and various modifications can be made within the scope of the invention. For example, the invention can be applied to not only the above-described various liquid crystal panels but also electroluminescence, plasma display devices.

thin film semiconductor device of invention is low priced and has high performance, and is thus optimum as an active matrix substrate of an active matrix liquid crystal display device. Particularly, the thin film semiconductor device is optimum as an active driver required to have matrix containing a performance.

A liquid crystal display device to which the invention is applied is low priced and has high performance, and is thus optimum as various displays including a full-color note PC.

The thin film electronic apparatus of the invention is inexpensive and has high performance, and will be thus widely used for general purposes.